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Synthesis and Structures of Triorganochalcogenium (Te, Se, S) Dinitramides

Thomas M. Klapötke,*[a] Burkhard Krumm,[a] and Matthias Scherr[a]

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The syntheses of the triorganochalcogenium dinitramide salts $[Ph_3Te][N(NO_2)_2]$ (**1**), $[Me_3Te][N(NO_2)_2]$ (**2**), $[Ph_3Se][N(NO_2)_2]$ (**3**), $[Me_3Se][N(NO_2)_2]$ (**4**), $[Ph_3S][N(NO_2)_2]$ (**5**), and $[Me_3S][N(NO_2)_2]$ (**6**), their characterization by multinuclear NMR spectroscopy, vibrational spectra, and single-crystal structures are described. The syntheses of the compounds were achieved with the help of $[Ag(py)_2][N(NO_2)_2]$ and $[Ag(NCCH_3)][N(NO_2)_2]$ as dinitramide transfer reagents. Whereas in the crystal structure of **1** different coordination modes to dinitramide moieties are present, the crystal structure of **3** shows only a single intermolecular contact to the dinitramide moiety.

Introduction

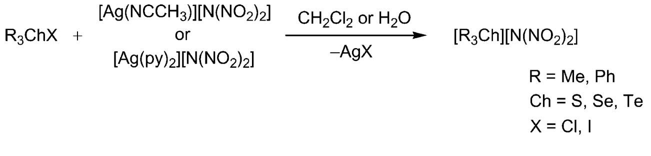
The dinitramide anion was first discovered by Russian chemists in 1971,[1] but was kept secret until it was independently rediscovered in the late 1980s in the USA.[2] Afterwards, the Russian work was summarized in a series of publications,[1,3–10] new aspects were added by different groups,[11–25] and also theoretical aspects of the dinitramide anion have been reported.[26–28] An overview of structural trends and variations in dinitramide salts has been given,[10,29,30] and potential applications for various dinitramide salts have been discussed.[31–33]

Within the last decades, triorganochalcogenium pseudohalides have been well investigated.[34–41] Our own contributions afforded a variety of triorganotelluronium/selenonium halides and pseudohalides,[42–44] among them the ionic azide compounds $[R_3Te]N_3$ and $[R_3Se]N_3$ (R = Me, Ph).[43,44] Continuing our efforts to explore the chemistry of main group elements with energetic substituents, in this contribution we report the first syntheses and crystal structures of triorganochalcogenium dinitramide salts.

Results and Discussion

The precursors for the syntheses of the triorganochalcogenium dinitramides $[R_3Ch][N(NO_2)_2]$ (Ch = Te, Se, S; R = Me, Ph) are the corresponding triorganochalcogenium halides. As dinitramide transfer reagents, the silver salts $[Ag(py)_2][N(NO_2)_2]$ (py = pyridine) and $[Ag(NCCH_3)][N(NO_2)_2]$ were chosen, as both can easily be prepared and are considerably safer to handle than the solvate-free compound $Ag[N(NO_2)_2]$.[21,45] The acetonitrile adduct is reported to consist of $[Ag(NCCH_3)_4][Ag_3\{N(NO_2)_2\}_4]$ in the solid state.[21] Although the reactions work with both silver dinitramide adducts, the use of $[Ag(NCCH_3)][N(NO_2)_2]$ is preferable than $[Ag(py)_2][N(NO_2)_2]$, not only because pyridine is a stronger base, but also because it is easier to remove acetonitrile in high vacuum than pyridine. In the course of our investigations, the molecular structure of the pyridinium dinitramide salt $[pyH][N(NO_2)_2]$ as a byproduct was obtained.[46] Because of the ease of formation of this pyridinium salt even in aprotic solvents, the use of the acetonitrile adduct is preferable. The disadvantage of the acetonitrile adduct is, that according to elemental analyses, the composition compared to reported $[Ag(NCCH_3)_4][Ag_3\{N(NO_2)_2\}_4]$ differs in the majority of cases. However, in order to add the exact stoichiometric amount of dinitramide to the starting materials, the latter composition had to be achieved before use.

The synthesis of triorganochalcogenium dinitramides **1**–**6** was achieved by reaction of the corresponding triorganochalcogenium halogenides with the dinitramide transfer reagent in dichloromethane or water (Scheme 1).



$$R_3ChX + \begin{matrix}[Ag(NCCH_3)][N(NO_2)_2] \\ \text{or} \\ [Ag(py)_2][N(NO_2)_2]\end{matrix} \xrightarrow[-AgX]{CH_2Cl_2 \text{ or } H_2O} [R_3Ch][N(NO_2)_2]$$

R = Me, Ph
Ch = S, Se, Te
X = Cl, I

Scheme 1. Preparation of triorganochalcogenium dinitramides.

The triphenyltelluronium(**1**)/selenonium(**3**) dinitramides are pale-yellow solids that decompose very slowly at ambient temperature over a period of two weeks, but are storable in the dark at temperatures below +4 °C for several months. In contrast to the products with the phenyl substituent, solvent evaporation of the compounds with the methyl group, $[Me_3Te][N(NO_2)_2]$ (**2**) and $[Me_3Se][N(NO_2)_2]$ (**4**), yielded

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[a] Department of Chemistry and Biochemistry, Ludwig-Maximilian University of Munich
Butenandtstr. 5-13(D), 81377 Munich, Germany
Fax: +49-89-2180-77492
E-mail: tmk@cup.uni-muenchen.de

oily products, which decompose more rapidly relative to the compounds with the phenyl substituent. In case the pyridine silver dinitramide transfer reagent is used for synthesis, present pyridine in the compounds can be removed by exposure to high vacuum at ambient temperature for two days.

According to the preparation of the telluronium and selenonium salts, the corresponding sulfonium salts, $[Ph_3S][N(NO_2)_2]$ (**5**) and $[Me_3S][N(NO_2)_2]$ (**6**), have also been prepared. In contrast to the viscous methyl-substituted compounds **2** and **4**, both organosulfonium dinitramides could be isolated as colorless solids. Compounds **5** and **6** are less stable relative to the corresponding organotelluronium and organoselenonium salts and decompose slowly at ambient temperature. However, both compounds can be stored at temperatures below –32 °C for several weeks without decomposition according to ^{14}N NMR spectroscopy.

The reaction of trimethyloxonium tetrafluoroborate with silver dinitramide was also performed, but no evidence for the formation of the desired trimethyloxonium dinitramide was found. According to the ^{14}N NMR spectrum of the solution, several resonances were found [major resonances: δ = –22 (NO_2 group) and –181 ppm], which could not be assigned properly. The simultaneous performed reaction of $[Me_3O][BF_4]$ with silver azide furnished, according to ^{14}N NMR spectroscopy, HN_3 as main product [δ = –136 (N_β), –177(N_γ), –324(N_α) ppm; CH_3CN solution]. Related to this finding, the main product of the reaction with silver dinitramide could possibly furnish dinitramine $HN(NO_2)_2$. However, no evidence for this compound could be found. In order to find evidence for the formation of $HN(NO_2)_2$, the reaction of CF_3SO_3H with $KN(NO_2)_2$ in dichloromethane as solvent was performed. The ^{14}N NMR spectrum of the solution yielded several resonances, whereas no resonance of the compared reaction of $[Me_3O][BF_4]$ with $Ag(py)_2N(NO_2)_2$ could be found. Instead N_2O [δ = –148 (N*N*O), –232 (*N*NO) ppm] and HNO_3 (δ = –41 or –51 ppm) as main products, likely the decomposition products of generated $HN(NO_2)_2$, could be identified by ^{14}N NMR spectroscopy. Finally, we were not able to identify the products of the reaction of $[Me_3O][BF_4]$ with silver dinitramide, but likely can exclude the formation of the protonated species $HN(NO_2)_2$, as it was found with HN_3 for the corresponding reaction with silver azide.

Spectroscopic Data

The salt-like nature of **1**–**6** could be confirmed by spectroscopic characterization (overview Table 1). In the ^{14}N NMR spectra two resonances were observed for the anion. Whereas a sharp resonance for the nitro group appears between δ = –11 and –14 ppm; the resonance for the amino nitrogen atom is found as a broad resonance in the range between δ = –55 and –59 ppm. This is comparable with literature values of the alkali salts of dinitramide (nitro group δ = –12 to –14 ppm, amino nitrogen atom δ = –58 to –62 ppm; all measured in D_2O)[24] and leads to the conclusion that in solution all compounds are completely dissociated. In the ^{125}Te NMR spectrum the resonance of the triphenyltelluronium cation in **1** is detected at δ = 788 ppm ($CDCl_3$), whereas the resonance of the trimethyltelluronium cation in **2** is shifted to higher field (δ = 439 ppm, D_2O). The same trend is observed for the selenonium cations in their ^{77}Se NMR spectra (**3**: δ = 498 ppm, $CDCl_3$; **4**: δ = 260 ppm, [D$_6$]acetone/δ = 256 ppm, CD_3CN). As expected,

Table 1. NMR resonances of triorganochalcogenium dinitramides (δ in ppm).

Compound	Solvent	^{125}Te	^{77}Se	^{14}N [N(*N*O$_2$)$_2$/ *N*(NO$_2$)$_2$]
$[Ph_3Te][N(NO_2)_2]$ (**1**)	$CDCl_3$	788		–13/–56 (br.)
$[Me_3Te][N(NO_2)_2]$ (**2**)	D_2O	439		–14/–58 (br.)
$[Ph_3Se][N(NO_2)_2]$ (**3**)	$CDCl_3$		498	–12/–56 (br.)
$[Me_3Se][N(NO_2)_2]$ (**4**)	[D$_6$]acetone		260	–11/–58 (br.)
	CD_3CN		256	–11/–55 (br.)
$[Ph_3S][N(NO_2)_2]$ (**5**)	$CDCl_3$			–11/–58 (br.)
$[Me_3S][N(NO_2)_2]$ (**6**)	[D$_6$]acetone			–10/–55 (br.)
	D_2O			–14/–59 (br.)

Table 2. Assignments of the observed IR and Raman bands for the dinitramide anions of **1**–**6** in cm^{-1} (ip = in phase, oop = out of phase).

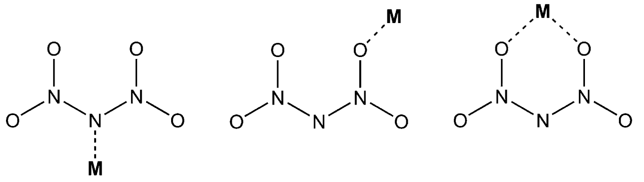
	1		**2**		**3**		**4**		**5**		**6**	
	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR
$\nu_{as}(NO_2)_{ip}$	1575	1582 (w)	1569		1574	1572 (m)			1579	1579 (m)		
		1572 (m)										
$\nu_{as}(NO_2)_{oop}$		1499 (vs)	1425	1406	1421	1499 (vs)	1426	1528 (vs)	1448	1504 (vs)	1424	1505 (vs)
		1441 (vs)				1421 (vs)		1431 (vs)		1425 (s)		
$\nu_{sym}(NO_2)_{ip}$	1335	1319 (s)	1329		1331	1320 (s)	1328	1343 (s)	1328	1346 (s)	1332	1334 (m)
$\nu_{sym}(NO_2)_{oop}$	1168	1196 (vs)	1191	1206 (w)	1162	1196 (vs)		1179 (vs)	1185	1174 (vs)	1189	1198 (vs)
		1171 (vs)				1170 (vs)						
$\nu_{as}(N_3)$	1022	1009 (vs)	1024		1024	1009 (vs)		1022 (vs)	1025	1064 (m)	1044	1045 (m)
		991 (vs)				991 (vs)		979 (s)		993 (s)		
$\nu_s(N_3)$		919 (s)		912 (s)		918 (s)		908 (w)		923 (m)	952	940 (s)
$\delta_{sciss}(NO_2)_{ip}$	828	822 (m)	827		825	822 (m)	825	828 (m)	827	830 (m)	828	826 (m)
$\delta_{rock}(NO_2)_{ip/oop}$		747 (vs)		751 (vs)		738 (vs)		761 (s)		743 (vs)		755 (vs)
$\delta_{sciss}(NO_2)_{oop}$		738 (vs)										
$\delta_{wag}(NO_2)_{ip}$	464	478 (m)	473	477 (m)	471	478 (m)	483	470 (w)	471	478 (m)	476	477 (m)
		471 (s)		470 (s)		470 (s)				470 (s)		470 (s)
$\delta_{wag}(NO_2)_{oop}$		457 (m)		456 (m)		457 (m)				457 (m)		457 (m)

all resonances of the cations are very similar to the resonances of the starting materials ([Ph$_3$Te]Cl δ = 759 ppm, CDCl$_3$; [Me$_3$Te]Cl δ = 441 ppm, D$_2$O; [Ph$_3$Se]Cl δ = 481 ppm, CDCl$_3$; [Me$_3$Se]I δ = 251 ppm, D$_2$O) and also comparable to known chalcogenium compounds such as the previously reported azides [Ph$_3$Te]N$_3$ (δ = 795 ppm, CDCl$_3$), [Me$_3$Te]N$_3$ (δ = 456 ppm, D$_2$O),[43] [Ph$_3$Se]N$_3$ (δ = 510 ppm, CDCl$_3$), and [Me$_3$Se]N$_3$ (δ = 251 ppm, D$_2$O).[44] The ^{13}C and ^{1}H NMR spectra have also been recorded for all compounds and display the expected resonances for phenyl and methyl-substituted compounds, respectively (for assignments see Exp. Sect.).

Compounds **1**–**6** were also characterized by their IR and Raman spectra. For all compounds the characteristic bands for the dinitramide anion were found and listed in Table 2. Some fundamental vibrations show splittings, caused by slight distortions and asymmetry of the structural variable nitro groups. Moreover, the vibrational spectra of the solids are dependent on the counterion. The comparison of the experimental detected bands with previously reported observed and calculated values[12,10] leads to an overall reasonable agreement.

Crystal Structures

The potential coordination modes for the dinitramide anion have been reported earlier and include monodentate coordination to the central nitrogen atom of the dinitramide skeleton, monodentate coordination to one oxygen atom of the nitro groups, and bidentate coordination to two oxygen atoms of the terminal nitro groups (Scheme 2).[11]



Scheme 2. Potential coordination modes for the dinitramide anion (analogue to ref.[11]).

Recently we presented an example for monodentate coordination mode to the central nitrogen atom and also for chelate-type coordination by two oxygen atoms in [pyH][N(NO$_2$)$_2$] and Li[N(NO$_2$)$_2$]·2H$_2$O, respectively.[46] Compound **1** crystallizes in the monoclinic crystal system, space group $P2_1/n$ with four molecules in the asymmetric unit. The molecules exist in the first order as cation–anion pairs with bidentate coordination of two oxygen atoms of the dinitramide anion (Figure 1).

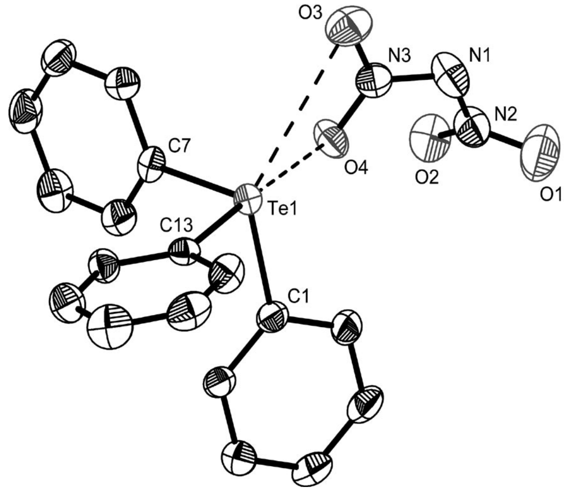


Figure 1. ORTEP plot of the molecular structure of **1**; H atoms omitted for clarity; selected bond lengths [Å] and angles [°]: Te1–C1 2.112(4), Te1–C7 2.121(4), Te1–C13 2.112(4), Te1···O3 3.493(3), Te1···O4 2.952(6), C1–Te1–C7 98.83(14), C1–Te1–C13 93.59(15), C7–Te1–C13 97.67(14), O3···Te1···O4 38.03(7).

The intermolecular Te···O distances are 3.349(3) and 2.952(6) Å and are significantly shorter than the sum of the tellurium–oxygen van der Waals radii (vdWr TeO 3.6 Å[47]). The tellurium–carbon bond lengths are in the range between 2.11 and 2.12 Å and are together with the resulting bond angles in good agreement with previously reported triphenyltelluronium cations.[39,43] Taking only the tellurium–carbon bonds into account, a typical trigonal-pyramidal arrangement (AX$_3$E) around the central tellurium atom is formed. Besides the mentioned contacts to the dinitramide moiety of the asymmetric unit, two further intermolecular contacts to symmetry generated dinitramide anions exist, which also have to be considered. The contacts are shown in Figure 2 and exhibit Te···O distances of 3.414(1) [Te1···O1(i)/Te1(ii)···O1(iii)] and 3.089(9) Å [Te1···O3(ii)/Te1(ii)···O3].

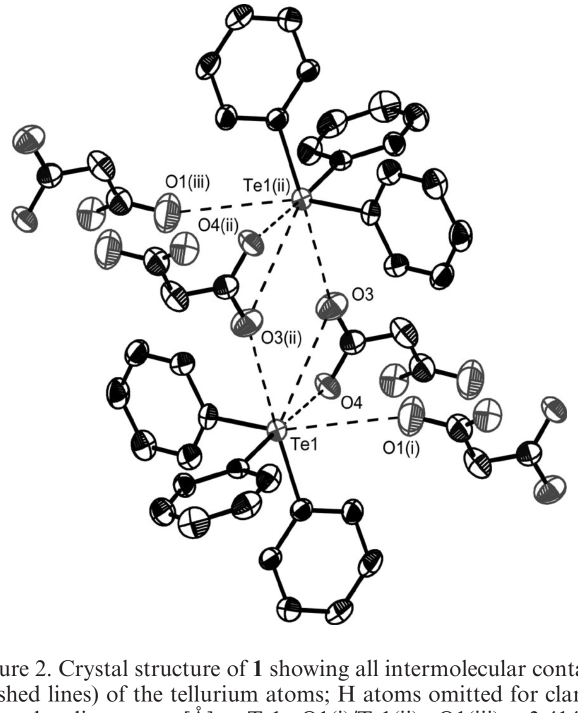


Figure 2. Crystal structure of **1** showing all intermolecular contacts (dashed lines) of the tellurium atoms; H atoms omitted for clarity; selected distances [Å]: Te1···O1(i)/Te1(ii)···O1(iii) 3.414(1), Te1···O3(ii)/Te1(ii)···O3 3.089(9), with i = 1 – *x*, –*y*, 1 – *z*; ii = –*x*, –*y*, 1 – *z*; iii = –1 + *x*, *y*, *z*.

This leads to a distorted capped octahedral coordination around the tellurium atom (coordination number seven) without taking the free valence electron pair of the tellurium atom into account. In addition to the aforementioned bidentate contacts to the dinitramide moiety monodentate contacts also exist to two additional dinitramide moieties, which lead to a 3D layered structure.

In contrast to telluronium salt **1**, selenonium salt **3** consists of isolated cation–anion pairs with only monodentate chalcogen–oxygen contacts (Figure 3). The compound also crystallizes in the monoclinic crystal system and in the same space group ($P2_1/n$) relative to the analogous telluronium compound.

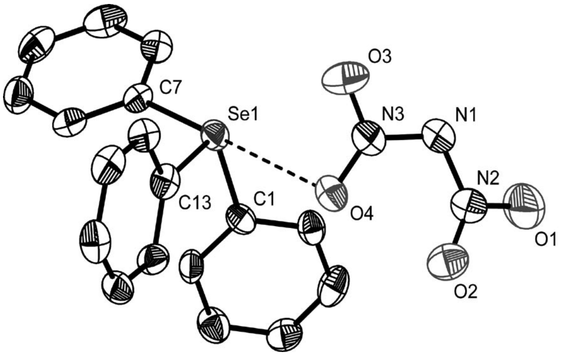


Figure 3. ORTEP plot of the molecular structure of **3**; H atoms omitted for clarity; selected bond lengths [Å] and angles [°]: Se1–C1 1.927(4), Se1–C7 1.930(4), Se1–C13 1.919(4), Se1···O4 2.979(4), C1–Se1–C7 98.02(16), C1–Se1–C13 103.41(16), C7–Se1–C13 101.03(16).

The selenium–carbon bond lengths are in the range between 1.92 and 1.93 Å and comparable to the previously reported [Ph_3Se]N_3 [1.915(4) Å].[48] The intermolecular selenium–oxygen distance is with 2.979(4) Å significantly shorter than the sum of the selenium–oxygen van der Waals radii (vdWr SeO 3.4 Å). This intermolecular contact leads to a distorted trigonal–bipyramidal coordination (AX_4E) around the selenium atom. No further intermolecular contacts below the sum of the van der Waals radii of the elements are present. This is in contrast to the structure of telluronium salt **1** and likely an effect of the smaller size of a selenium atom compared to a tellurium atom. The same behavior has been reported previously for the comparable azide salts [Ph_3Te]N_3 and [Ph_3Se]N_3.[43,48] Whereas in the crystal structure of the telluronium salt various intermolecular Te···N contacts are present, the structure of the selenonium salts consists of isolated cation–anion pairs with no significant interactions.

In both crystal structures the dinitramide anions exhibit the expected geometry with no intramolecular symmetry, that is, C_1 symmetry. The only known examples for intramolecular symmetry are to the best of our knowledge Li[$N(NO_2)_2$],[13] Li[$N(NO_2)_2$]·$2H_2O$[46] (both imposed C_2 symmetry), and 3,3-dinitroazetidinium[17] (imposed mirror plane). The nitro twist angles in **1** and **3** range from 19.7 to 33.9°, and the nitro bend angles are in the range between 5.4 and 6.6°, whereas the minimum O···O contact between the nitro groups are 2.585 Å (for **1**) and 2.551 Å (for **3**), respectively (see Table 3). These values are comparable to the structure of the ammonium salt of the dinitramide anion (ADN).[13]

Table 3. Selected twist and torsion angles for the dinitramide ion (for definitions, see refs.[13,30]).

Parameter	Te (**1**)	Se (**3**)
Twist (N2)	33.9	23.5
Twist (N3)	14.9	19.7
Bend (N2)	6.6	6.2
Bend (N3)	5.8	5.4
O···O	2.585	2.551
Torsion	45.9	41.2

In the course of our investigations we determined that our previously reported crystal system for [$Ag(py)_2$]-[$N(NO_2)_2$] is not triclinic,[21] but monoclinic with cell axes a = 6.1066(8) Å, b = 15.8561(16) Å, c = 13.934(2) Å and an angle of 99.250(12)° [V = 1331.7(3) Å^3], which could be achieved by transforming the reported b axis. This leads to the common space group $P2_1/c$ with four molecules in the asymmetric unit.

As a consequence of the herein reported successful syntheses of organochalcogenium dinitramides, the attempted preparation of covalent organochalcogen dinitramide compounds is currently underway and will be part of a future publication.

Experimental Section

General Remarks: All manipulation of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon by using flame-dried glass vessels or oven-dried plastic equipment and Schlenk techniques.[49] The solvents dichloromethane and acetonitrile were dried by standard methods, stored under an atmosphere of N_2, and freshly distilled prior to use. The telluronium/selenonium/sulfonium salts,[50–54,37,55,56,43,57] and the silver dinitramide salts[12,21] were prepared according to literature procedures. All reagents were used as received (Sigma–Aldrich, Acros Organics, Fluka, ABCR) if not stated otherwise. Preparation and usage of the silver salts was performed under exclusion of light. Infrared spectra were recorded with Perkin–Elmer Spektrum One FTIR or Nicolet 520 FTIR spectrometers (as neat liquids/solids or Nujol mulls between KBr plates), Raman spectra were recorded with a Perkin–Elmer 2000 NIR FT spectrometer fitted with a Nd-YAG laser (1064 nm) as neat solids or liquids. Mass spectra were recorded with a Finnigan MAT 95Q or a JEOL MStation JMS 700 spectrometer. Multiisotope-containing fragments refer to the isotope with the highest abundance (for example ^{130}Te, ^{80}Se). Elemental analyses C, H, N were performed with a Netsch STA 429 simultaneous thermal analyzer by the analytical service of the Department of Chemistry and Biochemistry, LMU. NMR spectra were recorded with a JEOL Eclipse 400 instrument, and chemical shifts were determined with respect to external Me_4Si (^{1}H, 399.8 MHz; ^{13}C, 100.5 MHz), $MeNO_2$ (^{14}N/^{15}N, 28.9/40.6 MHz), Me_2Se (^{77}Se, 76.3 MHz), and Me_2Te (^{125}Te, 126.1 MHz). Due to the temperature dependence of the ^{77}Se/^{125}Te NMR resonances, all samples were recorded at 25 °C. Yields of compounds **1**–**6** do not depend on the employed dinitramide transfer reagent and are in the range 90–98%. Elemental analyses could not be performed satisfactorily for all compounds and are therefore only reported where appropriate.

CAUTION! Silver dinitramide and dinitramide salts in general are potentially explosive. This necessitates meticulous safety precautions during their preparation and handling, please see ref.[58]

X-ray Crystallography: For all compounds an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection by using Mo-K_α radiation (λ = 0.71073 Å). The structures (Table 4) were solved by direct methods (SHELXS[59] or SIR97[60]) and refined by full-matrix least-squares on F^2 (SHELXL[59]). All non-hydrogen atoms were refined anisotropically. ORTEP plots are shown with thermal ellipsoids at the 50% probability level. CCDC-682940 (for **1**) and -682939 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal and structure refinement data.

	$[Ph_3Te][N(NO_2)_2]$ (**1**)	$[Ph_3Se][N(NO_2)_2]$ (**3**)
Empirical formula	$C_{18}H_{15}N_3O_4Te$	$C_{18}H_{15}N_3O_4Se$
Formula mass	464.93	416.29
Temperature [K]	200	200
Crystal size [mm]	0.29 × 0.20 × 0.09	0.21 × 0.11 × 0.02
Crystal description	pale-orange block	colorless platelet
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	9.0860(7)	9.1178(4)
b [Å]	14.6781(12)	14.0576(5)
c [Å]	13.4522(11)	13.6553(5)
β [°]	97.682(7)	95.361(4)
V [Å^3]	1778.0(2)	1742.60(12)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.737	1.587
μ [mm^{-1}]	1.702	2.184
F(000)	912	840
θ range [°]	4.1–26.0	3.7–26.0
Index ranges	$-10 \le h \le 12$ $-17 \le k \le 20$ $-11 \le l \le 18$	$-11 \le h \le 11$ $-16 \le k \le 17$ $-16 \le l \le 7$
Reflns. collected	9144	8928
Reflns. observed	2745	1795
Reflns. unique	3472 (R_{int} = 0.0391)	3422 (R_{int} = 0.0749)
*R*1, *wR*2 (2σ data)	0.0350, 0.0660	0.0375, 0.0625
*R*1, *wR*2 (all data)	0.0520, 0.0734	0.0847, 0.0724
Max./min. transm.	0.8621/0.7142	0.957/0.755
Data/restr./param.	3472/0/235	3422/0/235
GOOF on F^2	1.031	0.818
Larg. diff. peak/hole [e Å^{-3}]	1.293/–0.383	0.745/–0.353

General Procedure for the Preparation of Triphenyltelluronium/Selenonium/Sulfonium Dinitramide: To a solution of triphenyltelluronium/selenonium/sulfonium chloride/bromide (1.1 mmol) in dichloromethane (10 mL) was added $[Ag(NCCH_3)][N(NO_2)_2]$ or $[Ag(py)_2][N(NO_2)_2]$ (1.1 mmol) at 0 °C, and the mixture was stirred for 30 min. After additional stirring for 2 h at ambient temperature, the resulting precipitate (AgCl/AgBr) was filtered off, and all volatile materials of the remaining solution were removed in vacuo, yielding pale-yellow solids.

Triphenyltelluronium Dinitramide $[Ph_3Te][N(NO_2)_2]$ (1): Raman: $\tilde{\nu}$ = 3146 (10), 3063 (63), 1575 (34), 1335 (22), 1168 (12), 1022 (43), 1000 (100), 828 (18), 660 (47), 613 (13), 464 (9), 288 (30), 267 (47), 232 (44), 193 (27) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3447 (br.), 3092 (s), 3058 (s), 1582 (w), 1572 (m), 1499 (vs), 1441 (vs), 1319 (s), 1282 (m), 1196 (vs), 1171 (vs), 1069 (m), 1056 (m), 1009 (vs), 991 (vs), 919 (s), 822 (m), 747 (vs), 738 (vs), 683 (vs), 610 (m), 478 (m), 471 (s), 457 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.46–7.31 (m) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 133.8 ($^2J_{C,^{125}Te}$ = 35 Hz, *o*-C), 132.2 (*p*-C), 130.6 ($^3J_{C,^{125}Te}$ = 8 Hz, *m*-C), 122.4 ($^1J_{C,^{125}Te}$ = 245, $^1J_{C,^{123}Te}$ = 203 Hz, CTe) ppm. ^{14}N NMR (CDCl$_3$): δ = –13 [N(*N*O$_2$)$_2^-$], –56 [br., *N*(NO$_2$)$_2^-$] ppm. ^{15}N NMR (CDCl$_3$): δ = –12.9 [N(*N*O$_2$)$_2^-$] ppm. ^{125}Te{^{1}H} NMR (CDCl$_3$): δ = 788 [$^1J_{Te,^{13}C}$ = 245 Hz, $^1\Delta^{125}$Te ($^{12/13}$C) = 80.3 ppb (10.1 Hz)] ppm. MS (FAB+): *m*/*z* (%) = 359 (100) [M]$^+$, 282 (8) [M – Ph]$^+$, 205 (4) [M – 2Ph]$^+$. $C_{17}H_{15}N_3O_4Te$ (464.92): calcd. C 46.5, H 3.3, N 9.0; found C 46.6, H 3.2, N 8.8.

Triphenylselenonium Dinitramide $[Ph_3Se][N(NO_2)_2]$ (3): Raman: $\tilde{\nu}$ = 3146 (12), 3070 (76), 1574 (41), 1421 (11), 1331 (35), 1162 (16), 1071 (18), 1024 (53), 1002 (100), 825 (20), 672 (39), 611 (19), 471 (13), 338 (14), 316 (28), 247 (49), 217 (21) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3435 (br.), 3092 (s), 3058 (s), 2999 (m), 1667 (w), 1572 (m), 1499 (vs), 1421 (vs), 1320 (s), 1281 (m), 1196 (vs), 1170 (vs), 1069 (m), 1009 (vs), 991 (vs), 918 (s), 842 (w), 822 (m), 738 (vs), 683 (vs), 610 (m), 478 (m), 470 (s), 457 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.60–7.40 (m) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 133.3 (*p*-C), 131.2 ($^3J_{C,^{77}Se}$ = 6 Hz, *m*-C), 130.4 ($^2J_{C,^{77}Se}$ = 16 Hz, *o*-C), 125.5 ($^1J_{C,^{77}Se}$ = 83 Hz, CSe) ppm. ^{14}N NMR (CDCl$_3$): δ = –12 [N(*N*O$_2$)$_2^-$], –56 [br., *N*(NO$_2$)$_2^-$] ppm. ^{77}Se{^{1}H} NMR (CDCl$_3$): δ = 498 [$^1J_{Se,^{13}C}$ = 83 Hz, $^1\Delta^{77}$Se ($^{12/13}$C) = 72.5 ppb (5.5 Hz)] ppm. MS (FAB+): *m*/*z* (%) = 311 (47) [M]$^+$, 234 (11) [M – Ph]$^+$, 154 (100) [M – 2Ph]$^+$. $C_{17}H_{15}N_3O_4Se$ (416.28): calcd. C 51.9, H 3.6, N 10.1; found C 51.8, H 3.6, N 10.0.

Triphenylsulfonium Dinitramide $[Ph_3S][N(NO_2)_2]$ (5): Raman: $\tilde{\nu}$ = 3155 (8), 3067 (81), 1579 (69), 1508 (5), 1448 (6), 1328 (19), 1292 (6), 1185 (12), 1166 (12), 1078 (40), 1067 (22), 1025 (63), 1002 (100), 949 (6), 827 (12), 704 (10), 688 (21), 612 (20), 471 (7), 428 (5), 256 (35), 223 (15) cm^{-1}. IR (neat): $\tilde{\nu}$ = 3059 (m), 1750 (w), 1701 (w), 1674 (w), 1579 (m), 1504 (vs), 1474 (vs), 1444 (vs), 1425 (s), 1346 (s), 1291 (w), 1174 (vs), 1156 (vs), 1064 (m), 993 (s), 923 (m), 830 (m), 743 (vs), 702 (w), 679 (vs), 478 (m), 470 (s), 457 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.69–7.58 (m) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 134.6 (*p*-C), 131.5 (*m*-C), 130.8 (*o*-C), 123.8 (CS) ppm. ^{14}N NMR (CDCl$_3$): δ = –11 [N(*N*O$_2$)$_2^-$], –58 [br., *N*(NO$_2$)$_2^-$] ppm.

General Procedure for the Preparation of Trimethyltelluronium/selenonium/sulfonium Dinitramide: To a solution of trimethyltelluronium/selenonium/sulfonium chloride/iodide (1.1 mmol) in water (10 mL) was added $[Ag(NCCH_3)][N(NO_2)_2]$ or $[Ag(py)_2][N(NO_2)_2]$ (1.1 mmol) at 0 °C, and the mixture was stirred for 30 min. After additional stirring for 6 h at ambient temperature, the resulting precipitate (AgCl/AgI) was filtered off, and all volatile materials of the remaining solution were removed in vacuo, yielding pale-yellow oils (**2** and **4**) and a solid (**6**).

Trimethyltelluronium Dinitramide $[Me_3Te][N(NO_2)_2]$ (2): Raman: $\tilde{\nu}$ = 3031 (10), 3013 (8), 2919 (20), 1569 (34), 1425 (14), 1329 (41), 1191 (12), 1051 (15), 1024 (62), 1008 (88), 827 (28), 548 (100), 539 (97), 473 (34) 237 (11) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3423 (br.), 3010 (m), 2916 (m), 1631 (m), 1406 (s), 1234 (w), 1206 (w), 912 (s), 861 (w), 832 (w), 751 (vs), 539 (m), 477 (m), 470 (s), 456 (m) cm^{-1}. ^{1}H NMR (D$_2$O): δ = 2.38 ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 5.0 ppm. ^{14}N NMR (CDCl$_3$): δ = –14 [N(*N*O$_2$)$_2^-$], –58 [br., *N*(NO$_2$)$_2^-$] ppm. ^{125}Te{^{1}H} NMR (D$_2$O): δ = 439 ppm. FAB$^+$ MS: *m*/*z* (%) = 173 (100) [M$^+$].

Trimethylselenonium Dinitramide $[Me_3Se][N(NO_2)_2]$ (4): Raman: $\tilde{\nu}$ = 3035 (38), 2939 (77), 1426 (24), 1328 (51), 825 (36), 607 (74), 585 (100), 483 (22) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3441 (br.), 3019 (m), 2913 (w), 1629 (m), 1528 (vs), 1431 (vs), 1384 (m), 1343 (s), 1293 (m), 1179 (vs), 1022 (vs), 979 (s), 953 (m), 908 (w), 828 (m), 761 (s), 732 (s), 575 (w), 470 (w) cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 2.93 ppm. ^{1}H NMR (CD$_3$CN): δ = 2.69 ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 22.2 ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ = 22.4 ppm. ^{14}N NMR ([D$_6$]-acetone): δ = –11 [N(NO$_2$)$_2^-$], –58 [br., N(NO$_2$)$_2^-$] ppm. ^{14}N NMR (CD$_3$CN): δ = –11 [N(NO$_2$)$_2^-$], –55 [br., N(NO$_2$)$_2^-$] ppm. ^{77}Se{^{1}H} NMR ([D$_6$]acetone): δ = 260 ppm. ^{77}Se{^{1}H} NMR (CD$_3$CN): δ = 256 ppm. MS (FAB+): m/z (%) = 126 (100) [M]$^+$.

Trimethylsulfonium Dinitramide [Me$_3$S][N(NO$_2$)$_2$] (6): Raman: $\tilde{\nu}$ = 3023 (47), 2933 (100), 1511 (10), 1424 (23), 1332 (52), 1189 (9), 1044 (13), 952 (14), 828 (35), 734 (51), 658 (84), 476 (21), 291 (41) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3019 (m), 2934 (w), 1505 (vs), 1416 (s), 1349 (w), 1334 (w), 1198 (vs), 1045 (m), 996 (vs), 940 (m), 826 (m), 755 (s), 719 (m), 477 (m), 470 (s), 457 (m) cm^{-1}. ^{1}H NMR (D$_2$O): δ = 2.87 ppm. ^{1}H NMR ([D$_6$]acetone): δ = 3.12 ppm. ^{13}C{^{1}H} NMR (D$_2$O): δ = 27.0 ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 29.8 ppm. ^{14}N NMR (D$_2$O): δ = –14 [N(NO$_2$)$_2^-$], –59 [br., N(NO$_2$)$_2^-$] ppm. ^{14}N NMR ([D$_6$]acetone): δ = –10 [N(NO$_2$)$_2^-$], –55 [br., N(NO$_2$)$_2^-$] ppm.

Attempted Preparation of Trimethyloxonium Dinitramide [Me$_3$O][N(NO$_2$)$_2$]: To a solution of trimethyloxonium tetrafluoroborate (0.7 mmol) in dichloromethane (3 mL) was added [Ag(NCCH$_3$)][N(NO$_2$)$_2$] or [Ag(py)$_2$][N(NO$_2$)$_2$] (0.7 mmol) at 0 °C, and the mixture was stirred for 50 min. After that period a colorless precipitate, insoluble in common organic solvents, was obtained and a sample of the colorless supernatant for the NMR experiment was taken. In that sample no evidence for the formation of [Me$_3$O][N(NO$_2$)$_2$] was found.

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